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ABSTRACT

A systematic investigation has been made of the extraction of metallic salts and complexes by organic solvents. The conditioning agents employed in the survey included ethylenediamine, ethylenediaminetetraacetic acid, mannitol, hydrochloric acid, potassium iodide, ammonium thiocyanate, pyridine, perchloric acid, acetic acid and malonic acid. The solvents used were n-butyl chloride, petroleum ether, benzene, n-amyl alcohol, chloroform, methyl isopropyl ketone, isopropyl ether, butyraldehyde, carbon tetrachloride and ethyl acetate. Methyl isopropyl ketone and butyraldehyde were found to be very good solvents for the extraction of metallic complexes. Only those solvents used which contained oxygen were found to extract the complexes included in this study. Several extractions were discovered which hold promise for application in qualitative and quantitative analysis.

The extraction of lead iodide with methyl isopropyl ketone has been thoroughly investigated as a part of these studies. It has been found that when lead solutions are treated with a large excess of potassium iodide and adjusted to the proper acidity, lead iodide can be extracted with methyl isopropyl ketone. The extraction performed in this manner was 97% complete in a single pass. Interferences were kept at a minimum through the use of a preliminary extraction which was applied after treating the aqueous solution with ammonium thiocyanate and hydrochloric acid.

The pararosaniline hydrochloride test for gold was rendered specific for that metal by extracting an acidic aqueous solution of auric chloride with ethyl acetate. In this manner, gold was separated from the platinum metals, a group which constituted the principal interference in the

detection of gold. After the separation of phases the organic layer was evaporated, taken up with a few drops of water and applied to the reagent on spot test paper. The test was found to be sensitive to 5 gamma of gold.

A device was needed for the rapid extraction of small volumes of aqueous solutions with only a few drops of organic solvent. An extraction pipet was designed and prepared and has served quite well in this capacity.

INTRODUCTION

The use of extraction techniques as a means of effecting analytical separations has for many years provided the chemist with a very useful tool, and especially in recent years have these techniques become generally popular. The increased interest in this field can be attributed in part to the appearance of a considerable number of extraction devices, such as the countercurrent extractors discussed annually in the review articles of Craig (6, 7, 8), and the development of numerous colorimetric procedures based on the extraction of organic-metallic complexes (13, 23, 24, 27, 32). The extraction of inorganic complexes also holds many interesting possibilities, and the applications of these extractions to analytical separations, as well as to colorimetric procedures, are to be found throughout the literature. It is with the extraction of inorganic complexes that this investigation is primarily concerned.

Before embarking upon a discussion of the experimental work and the results of this investigation it might be well to discuss the various classes of extractions and the uses to which they have been put.

Generally, extractions can be classified according to the following categories: liquid-liquid, liquid-solid, liquid-gas and solid-gas. Because this study was confined to liquid-liquid systems only brief mention will be made of the other classifications.

Probably the most familiar type of liquid-liquid extraction being employed in analytical chemistry is that in which a particular component of an aqueous mixture is extracted into an organic solvent with the formation of a highly colored organic phase which is then readily adapted to

a photometric analysis. In such a manner cobalt can be determined after treating it with ammonium thiocyanate and extracting it with amyl alcohol (18, 19, 28). The blue color of the thiocyanate complex is sufficiently intense to provide an excellent means of determining cobalt colorimetrically. Similarly, iron can be extracted as the thiocyanate complex by a mixture of amyl alcohol and ethyl ether (33, 35); the blood red color of the organic phase is then measured photometrically after the separation of phases. The thiocyanate of molybdenum can be extracted by normal butyl acetate with the formation of a reddish-brown color. A colorimetric determination of molybdenum based on this extraction has been reported by James (13). Colorimetric procedures have been developed for the determination of bismuth, both as the thiocyanate complex (34) and as the iodide complex (12). In the former procedure amyl alcohol was employed as solvent, and in the latter a 3:1 mixture of amyl alcohol and ethyl acetate was used. One of the more outstanding examples of the use of extraction techniques in colorimetric procedures is the determination of chromium by extracting the blue perchromic acid and measuring the intensity of the blue extract. Amyl acetate has been used in a procedure reported by Bishop and Dwyer (1).

There are two principal advantages of employing an extraction procedure in colorimetric analyses. First, in many cases the desired component is separated from color masking or reaction masking interferences; and second, small amounts of material can be easily concentrated from relatively dilute solutions. Except for the elimination of color masking interferences, the advantages listed above are manifest in all procedures employing extraction techniques.

The second group is comprised of extractions which can be utilized also to isolate a desired component without depending upon the development of a color. The importance of such a general separation technique is becoming increasingly apparent, and by employing extraction in conjunction with complexing agents many of the qualitative and quantitative analyses of metallic ions could be greatly improved with regard to sensitivity. Many of the metal chlorides are extractable from hydrochloric acid solution using diethyl ether (25). It has been reported that ferric chloride is extracted better and over wider ranges of concentration when isopropyl ether is used as solvent (9). Uranium and thorium nitrates have been extracted by ethyl ether (22). Zinc is extracted by ethyl ether as the thiocyanate in the dithizone detection of zinc reported by Vanossi (36). Mercury can be determined gravimetrically after extraction of the iodide by ethyl ether (17). The extract is evaporated and the mercury weighed as mercuric iodide. Thallium is separated from lead, silver and bismuth by extracting the bromide with butyl acetate (20). Gold can be separated from the platinum metals by extracting the chloride into ethyl acetate (16). Pentavalent antimony may be separated from trivalent antimony by extracting a hydrochloric acid solution of these ions with isopropyl ether (10). Pentavalent antimony is extracted almost 100% while trivalent antimony is less than 2% extracted.

A third group which involves two immiscible liquids, but which does not represent true extraction, is one in which a precipitate is formed and is gathered at the interface when an organic solvent is shaken with the aqueous solution. Examples of the use of such methods are found both

in qualitative and quantitative analysis. Ammoniacal solutions of zinc, when treated with resorcinol, produce a blue precipitate. The detection of zinc in low concentrations is facilitated by shaking the aqueous solution with ether, which causes the precipitate to settle at the interface (25). Mercury is detected by the violet precipitate produced on the addition of cryogenin; sensitivity is increased when benzene is added and the precipitate is collected at the interface (2). Nickel is detected as the dimethylglyoxime complex with maximum sensitivity when the aqueous solution of the precipitate is shaken with carbon tetrachloride, thus collecting the precipitate at the interface (14). Silver and chloride determinations by the Volhard method may employ benzene as a collecting agent to prevent the interference of the silver chloride precipitate in detecting the end point of the titration (5). In the iodometric determination of selenium, benzene is added to gather the reduced selenium at the interface to prevent its interference in the perception of the end point of the titration (31).

The extraction of a particular component from a solid mixture by an organic solvent provides a method of separation which in many cases is quite selective. Generally, the techniques involved are time consuming, requiring the conversion of the desired constituent into the salt form in which it is extracted. In spite of this limitation, solid-liquid extractions offer a means of separating some ions which are difficult to separate by other means. Lithium can be separated from sodium and potassium by extraction of the anhydrous chlorides with amyl alcohol (21). The alkali and alkaline earth bromides can be separated into two groups by extracting the dry residue of these salts with amyl alcohol (4). Lithium, calcium, strontium and magnesium comprise one group while the other members constitute the other group. Lithium stearate

can be determined turbidimetrically due to its insolubility in amyl alcohol, in which the other alkali metals are soluble (38). Miller and Traves (21) report the separation of calcium and sodium from potassium by the extraction of their perchlorates by amyl alcohol, potassium perchlorate being insoluble in the alcohol. Aluminum nitrate can be separated from beryllium nitrate by extracting the solid mixture of these salts with amyl alcohol. Beryllium nitrate is soluble in this solvent, whereas aluminum nitrate is not (3).

The extraction of a particular component of a gaseous mixture by passing the mixture over a solid adsorbent is a familiar laboratory practice which exemplifies the solid-gas type of extraction. The uses of calcium chloride and ascarite in adsorption trains to remove water vapor and carbon dioxide, respectively, are good examples of the solid-gas extraction system (29).

The analysis of gaseous mixtures by means of the Orsat apparatus (30) provides the best example of the liquid-gas extraction system. An alkaline pyrogallol solution is used to extract the oxygen from a gaseous mixture of known volume, and potassium hydroxide solution is employed to extract carbon dioxide from the mixture. Carbon monoxide is extracted by means of a solution of cuprous chloride.

From the preceding paragraphs the importance and usefulness of extraction techniques in analytical separations can readily be seen. The study reported in the following pages is the result of a systematic investigation which was made in an effort to obtain information regarding the efficiency of some of the solvents which have not been extensively employed in extraction procedures, and to discover, if possible, some extractable inorganic and organic salts of complexes which might find use in analytical determinations. The solvents

included in the systematic study were chosen to represent as many classes of organic compounds as possible and also to include at least one member of four classes of solvents proposed by Ewell, Harrison and Berg (11). These four classifications are based on the tendency of the solvent to form hydrogen bonds with the material extracted and consist of the hydrogen donor type solvent, the hydrogen acceptor type solvent, the hydrogen acceptor-donor type solvent and the solvents which do not enter into hydrogen bond formation.

The conditioning agents were selected to include a large group of the ions commonly employed as complex formers. Obviously, some limit had to be imposed on the number of both conditioning agents and solvents used in the study. Originally, ten solvents and nine conditioning agents were decided upon but as the study progressed it developed that the extraction of some other complexes might prove interesting. So it was that upon the completion of the original survey pyridine was added to the list of conditioning agents.

Immediately following the report of the extraction study appears a description of the experiments performed in the investigation of one of the systems resulting from the original study, the extraction of lead iodide by methyl isopropyl ketone. This investigation is presented in the form in which it was submitted for publication.

Reprints of two published works appear as the final portion of this dissertation. Both papers are concerned with the application of extraction methods to analytical chemistry. It was the neatness and rapidity of the extraction procedure used in the isolation of gold which prompted the systematic investigation of the extraction of metallic complexes by organic solvents.

An Experimental Survey of the Extraction of Metallic Complexes with Organic Solvents

EXPERIMENTAL

The organic solvents employed in the extraction study are listed in Table I. The solvents were limited to those which did not tend to form emulsions and which were at most only partially miscible with water. In addition, the lowest boiling immiscible, or partially miscible, member of a class was selected in order to facilitate evaporation when this technique was required before testing for the presence of the extracted complex.

Chloroform represents the hydrogen donor type solvent mentioned earlier, methyl isopropyl ketone the hydrogen acceptor type, butyraldehyde the acceptor-donor type and benzene the type of solvent which does not enter into hydrogen bond formation. Benzene, chloroform, carbon tetrachloride and ethyl acetate were available as reagent grade chemicals. Methyl isopropyl ketone, isopropyl ether, n-amyl alcohol, n-butyl chloride and butyraldehyde were redistilled.

As stated previously, the conditioning agents were chosen on the basis of their ability to form complex ions and molecules. A list of these complex formers is found in Table II. Ethylenediamine, ethylenediaminetetraacetic acid, perchloric acid, hydrochloric acid, pyridine and acetic acid were used without dilution while mannitol, malonic acid, potassium iodide and ammonium thiocyanate were used as saturated solutions. The original intent of the investigation was to use each conditioning agent and each solvent with all of the common metal ions available in the laboratory. This would amount to one hundred extractions with each metal ion, and since thirty-one metal ions were included in the survey, the total

number of extractions attempted ran to thirty-one hundred. To have performed these extractions on a macro scale employing conventional equipment and techniques would have meant the use of quite large volumes of solvent as well as considerable loss of time in making separations and evaporations when these were required. In order to avoid this loss of time and solvent an extraction pipet was used which had previously been designed for the separation of minute amounts of gold from the platinum metals in a spot test for gold reported by West and Carlton (37). Using this pipet only 10-15 drops of solvent were required in each extraction, separations were effected rapidly, and when evaporations were necessary, a gentle blowing upon the surface of the solvent quickly accomplished this in most cases.

Because only a single ion was extracted in each case, very simple tests could be used in detecting the presence of the metal ion after extraction and separation of phases. If the organic phase was colored, two blanks were extracted for comparison; one contained only the metal ion and the other only the conditioning agent. In this way it was possible to determine whether the solvent reacted with the conditioning agent to produce a colored organic layer, or the metal ion was extractable directly, without conditioning. This latter possibility became manifest in some cases in which it was necessary to prepare the metal ion in acidic solution. Ordinarily, the aqueous phase was tested with the reagent and compared with a control containing the same amount of metal ion which was present in the aqueous phase before extraction. In the

cases in which extraction was suspected, but the organic layer was uncolored, the organic phase was evaporated and tested, or extracted with an aqueous solution of the reagent. In this manner a double check was obtained on the extraction and an estimate was then made on the degree to which the metal salt or complex was extracted. These extractions were classified as partial extraction (less than 50%), good extraction (50%-90%) and excellent extraction (greater than 90%).

The metal ions which were included in the extraction survey are listed in Table III, along with the test or tests used in their detection after extraction and separation of phases. The metal ions were prepared as 1% solutions. The procedure employed in the extraction survey was as follows: in a clean 5 milliliter beaker 2 drops of the conditioning agent and 2 drops of the test solution were mixed. To this was added 10-15 drops of solvent and the two layers were mixed thoroughly in an extraction pipet. In the event any color developed in the organic layer, a blank containing 2 drops of the metal ion and another blank containing 2 drops of the conditioning agent were extracted. The colors resulting from the last two extractions were compared with that of the first. If no color developed on the extraction of the conditioned metal ion each phase was passed into a separate 5 milliliter beaker and the reagent was added to the beaker containing the aqueous phase. The resulting color, or precipitate, was compared with that obtained by adding the reagent to a solution containing the amount of metal ion known to be present in the aqueous phase before extraction. If extraction was suspected, the organic phase was extracted with an aqueous solution of a suitable reagent. In

some instances there was reason to believe that a complex was extracted by the organic solvent which was more stable than the compound possible between the reagent and the metal ion. In those cases the organic phase was evaporated, taken up with 2 drops of concentrated nitric acid and evaporated again. After diluting with a few drops of water the reagent was added and the reaction observed. An estimation of the degree of extraction was made as proposed in an earlier paragraph.

The successful results of the extractions attempted by the procedure outlined above are found in Table IV through Table VII.

DISCUSSION OF RESULTS AND CONCLUSIONS

The study of the extraction of metal complexes revealed several very interesting phenomena. Some of the complexes developed colors in the organic phase which were much more intense than that present in aqueous solution. For example, bismuth iodide in methyl isopropyl ketone is a very dark reddish-orange while in the aqueous phase it has a yellow color. Copper thiocyanate in methyl isopropyl ketone is a very intense reddish-brown as compared to a much lighter color of the same hue in aqueous solution. Cobalt thiocyanate in aqueous media is a violet-pink, while in many organic solvents the color of the complex is a brilliant blue.

Also interesting is the way in which several precipitates in aqueous solution are readily dissolved in some organic solvents. Mercuric iodide provides an excellent example; the bright orange precipitate of mercuric iodide is quickly dissolved when shaken with methyl isopropyl ketone. The other oxygen containing solvents, with the exception of isopropyl ether, exhibit a similar solvent action toward this precipitate. Lead iodide, a yellow precipitate in aqueous solution, is soluble in methyl isopropyl ketone. When solutions of gold are treated with ammonium thiocyanate an orange precipitate is formed which is soluble in methyl isopropyl ketone, butyraldehyde, amyl alcohol and ethyl acetate.

The efficiency of the oxygen containing solvents in the extraction of metal complexes was still another very interesting phenomenon observed during the extraction study. Butyraldehyde, ethyl acetate, methyl isopropyl ketone and amyl alcohol were very good solvents while isopropyl

ether was only fair. Benzene, carbon tetrachloride, chloroform, n-butyl chloride and petroleum ether were observed to extract none of the complexes. Methyl isopropyl ketone appeared to be the best solvent employed in the study, although no quantitative experiments were performed to determine which solvent was actually the best extractant. It would be interesting to conduct experiments to show how the efficiency of extractants varies with chain length in a homologous series such as the methyl ketones. Similar experiments might be carried out with the aldehydes, the esters, the alcohols and the ethers.

Probably the most significant result of the extraction study was the realization that extraction, as a means of separation, offers so many and so varied possibilities for increased specificity in both qualitative and quantitative analysis. In the second portion of this report is presented a discussion of the extraction of lead iodide by methyl isopropyl ketone which serves as a good example of the use of extraction techniques as a means of isolating a particular ion. On a micro or semimicro scale, using the extraction pipet, two or three preliminary extractions may be performed in much less time than is required to execute a precipitation, filtration and washing. Many very sensitive tests reported in the literature might be made more selective through the use of a preliminary extraction designed to isolate the desired ion in either the organic or the aqueous phase.

At present, three systems are being investigated as a direct result of the extraction survey. These are the extraction of bismuth iodide

by methyl isopropyl ketone, the extraction of manganese with butyraldehyde after treatment with sodium tetraborate, and the extraction of perchromic acid with ethyl acetate.

TABLE I

Solvents Used in the Extraction Study

n-Butyl chloride	Methyl isopropyl ketone
Petroleum ether	Isopropyl ether
Benzene	Butyraldehyde
n-Amyl alcohol	Carbon tetrachloride
Chloroform	Ethyl acetate

TABLE II

Conditioning Agents Used in the Extraction Study

Ethylenediaminetetraacetic acid	Perchloric acid
Ethylenediamine	Potassium iodide
Mannitol	Hydrochloric acid
Malonic acid	Ammonium thiocyanate
Acetic acid	Pyridine

TABLE III

Metal Ions Included in the Extraction Survey

Metal Ion	Means of Detection
Li^{+}	Flame Test
Na^{+}	Zinc Uranyl Acetate
K^{+}	Flame Test
Cs^{+}	Flame Test
Ag^{+}	Chloride
	Sulfide
Au^{+++}	Visual
	Sulfide
Cu^{++}	Visual
	Ammonium Hydroxide
Fe^{+++}	Visual
	Ammonium Thiocyanate
Co^{++}	Visual
	Ammonium Thiocyanate
Ni^{++}	Visual
	Sulfide
Ba^{++}	Sulfate
Ca^{++}	Oxalate
Sr^{++}	Oxalate
Al^{+++}	Ammonium Hydroxide
Pb^{++}	Sulfate
	Sulfide

TABLE III
(continued)

Metal Ions Included in the Extraction Study

Metal Ion	Means of Detection
Pt^{++++}	Visual
Pd^{++}	Visual
Rh^{+++}	Visual
Ru^{+++}	Visual
Ir^{++++}	Visual
Cr^{+++}	Visual
	Perchromic Acid
UO_2^{++}	Visual
Bi^{+++}	Thiourea
Cd^{++}	Sulfide
Hg^{++}	Sulfide
Zn^{++}	Sulfide
Sn^{++++}	Sulfide
Mn^{++}	Peroxide
Sb^{+++}	Rhodamine B
As^{+++}	Sulfide

TABLE IV

Extractions Employing Potassium Iodide as Conditioning Agent

Metal Ion	Solvent	Extent of Extraction
Au^{+++}	Methyl isopropyl ketone	Excellent
	n-Amyl alcohol	Excellent
	Butyraldehyde	Excellent
	Ethyl Acetate	Excellent
Pb^{++}	Methyl isopropyl ketone	Partial
Bi^{+++}	Methyl isopropyl ketone	Excellent
	n-Amyl alcohol	Good
	Butyraldehyde	Good
	Ethyl acetate	Good
	Isopropyl ether	Partial
Hg^{++}	Methyl isopropyl ketone	Excellent
	n-Amyl alcohol	Good
	Butyraldehyde	Good
	Ethyl acetate	Good
Ru^{+++}	Methyl isopropyl ketone	Partial
	n-Amyl alcohol	Partial
	Butyraldehyde	Partial
	Ethyl acetate	Partial

TABLE IV
(continued)

Extractions Employing Potassium Iodide as Conditioning Agent

Metal Ion	Solvent	Extent of Extraction
Sb^{+++}	Methyl isopropyl ketone	Excellent
	n-Amyl alcohol	Good
	Butyraldehyde	Good
	Ethyl acetate	Good
Ir^{++++}	Methyl isopropyl ketone	Excellent
	n-Amyl alcohol	Excellent
	Butyraldehyde	Excellent
	Ethyl acetate	Excellent
Pd^{++}	Methyl isopropyl ketone	Excellent
	Butyraldehyde	Excellent
	n-Amyl alcohol	Good
	Ethyl acetate	Good
Cu^{++}	Methyl isopropyl ketone	Partial
	Butyraldehyde	Partial
	n-Amyl alcohol	Partial
	Ethyl acetate	Partial

TABLE V

Extractions Employing Ammonium Thiocyanate as Conditioning Agent

Metal Ion	Solvent	Extent of Extraction
Fe^{+++}	Methyl isopropyl ketone	Excellent
	n-Amyl alcohol	Good
	Butyraldehyde	Excellent
	Ethyl acetate	Good
	Isopropyl ether	Partial
Zn^{++}	Methyl isopropyl ketone	Good
	n-Amyl alcohol	Good
	Butyraldehyde	Good
	Ethyl acetate	Partial
	Isopropyl ether	Partial
Hg^{++}	Methyl isopropyl ketone	Good
	n-Amyl alcohol	Good
	Butyraldehyde	Good
	Ethyl acetate	Partial
	Isopropyl ether	Partial
Bi^{+++}	Methyl isopropyl ketone	Excellent
	n-Amyl alcohol	Good
	Butyraldehyde	Good
	Ethyl acetate	Partial
	Isopropyl ether	Partial

TABLE V
(continued)

Extractions Employing Ammonium Thiocyanate as Conditioning Agent

Metal Ion	Solvent	Extent of Extraction
UO_2^{++}	Methyl isopropyl ketone	Excellent
	Butyraldehyde	Excellent
	n-Amyl alcohol	Good
	Ethyl acetate	Partial
Ru^{+++}	Methyl isopropyl ketone	Good
	Butyraldehyde	Good
	n-Amyl alcohol	Partial
	Ethyl acetate	Partial
Pd^{++}	Methyl isopropyl ketone	Good
	Butyraldehyde	Good
	n-Amyl alcohol	Good
	Ethyl acetate	Partial
Pt^{++++}	Methyl isopropyl ketone	Partial
	Butyraldehyde	Partial
	n-Amyl alcohol	Partial
	Ethyl acetate	Partial
Co^{++}	Methyl isopropyl ketone	Excellent
	Butyraldehyde	Excellent
	n-Amyl alcohol	Excellent
	Ethyl acetate	Partial
Cu^{++}	Methyl isopropyl ketone	Good
	Butyraldehyde	Good
	n-Amyl alcohol	Partial
	Ethyl acetate	Partial

TABLE VI

Extractions Employing Hydrochloric Acid as Conditioning Agent

Metal Ion	Solvent	Extent of Extraction
Fe^{+++}	Methyl isopropyl ketone	Excellent
	Butyraldehyde	Excellent
	n-Amyl alcohol	Good
	Ethyl acetate	Partial
	Isopropyl ether	Partial
Au^{+++}	Methyl isopropyl ketone	Excellent
	Butyraldehyde	Excellent
	n-Amyl alcohol	Excellent
	Ethyl acetate	Excellent
	Isopropyl ether	Excellent
Pd^{++}	Methyl isopropyl ketone	Good
	Butyraldehyde	Good
	n-Amyl alcohol	Good
	Ethyl acetate	Partial
	Isopropyl ether	Partial
Ru^{+++}	Methyl isopropyl ketone	Partial
	Butyraldehyde	Partial
	n-Amyl alcohol	Partial
	Ethyl acetate	Partial

TABLE VI
(continued)

Extractions Employing Hydrochloric Acid as Conditioning Agent

Metal Ion	Solvent	Extent of Extraction
Sn^{++++}	Methyl isopropyl ketone	Good
	Butyraldehyde	Good
	n-Amyl alcohol	Good
	Ethyl acetate	Partial
	Isopropyl ether	Partial
Sb^{+++}	Methyl isopropyl ketone	Excellent
	Butyraldehyde	Excellent
	n-Amyl alcohol	Good
	Ethyl acetate	Good
	Isopropyl ether	Partial
As^{+++}	Methyl isopropyl ketone	Partial
	Butyraldehyde	Partial
	n-Amyl alcohol	Partial
	Ethyl acetate	Partial

TABLE VII

Extractions Employing Pyridine as Conditioning Agent

Metal Ion	Solvent	Extent of Extraction
Fe^{+++}	Butyraldehyde	Good
Cu^{++}	Butyraldehyde	Excellent
Co^{++}	Butyraldehyde	Good
Mn^{++}	Butyraldehyde	Good

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The Extraction of Lead Iodide by Methyl Isopropyl Ketone

Submitted to ANALYTICAL CHEMISTRY **for publication**

THE EXTRACTION OF LEAD IODIDE BY METHYL ISOPROPYL KETONE

by

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It is the purpose of this paper to inaugurate a series of studies dealing with the extraction of inorganic and organic complexes. In those cases in which colorimetric procedures are practical the procedures will be incorporated as a part of the paper or will be forthcoming. The use of extraction techniques in analytical separations has become increasingly popular in the last few years, particularly in those cases in which it is possible to selectively extract a desired component into an organic solvent and at the same time develop a highly colored organic phase which is readily adaptable to colorimetric procedures. Ordinarily, selectivity is accomplished through the use of complexing agents, careful control of the pH, or a combination of these conditions.

Organic reagents have been found to lend themselves readily to extraction procedures through the formation of chelate compounds which are soluble in organic solvents. The use of dithizone in the determination of lead offers one of the best and most familiar examples of organic reagents employed in this manner. Other organic reagents which have been utilized similarly for various metal extractions are 8-quinolinol, cupferron, o-nitrosophenol, sodium diethyldithiocarbamate and dimethylglyoxime, to name a few.

Separations based upon the extraction of inorganic salts are not as widely used although a few are quite familiar and are in general use. The authors have investigated the extraction of a number of inorganic complexes and have found iodide and thiocyanate complexes to be particularly susceptible to solution in organic solvents. Several of these produced colored organic phases of sufficient intensity to merit further investigation of the possibility of employing them in colorimetric procedures. The extraction of inorganic complexes as a rapid means of isolating a particular ion has a number of interesting applications both in eliminating interferences and in isolating desired constituents for subsequent color development and photometric measurement.

The extraction of lead iodide from acidic aqueous solutions has been found to be possible when the proper organic solvent was employed, the most efficient solvents being the ketones, and in particular, methyl isopropyl ketone. The removal of practically all interferences was accomplished by a preliminary extraction in which ammonium thiocyanate and hydrochloric acid were used to condition the aqueous solution and methyl isopropyl ketone was used as the solvent. After separation of the phases, the aqueous phase was treated with potassium iodide and again extracted with methyl isopropyl ketone. Lead iodide, under these conditions, was practically completely extracted with cadmium and ruthenium constituting the only interferences. By employing such a procedure, lead can be isolated from aqueous solutions of all the ions except cadmium and ruthenium and can be subsequently analyzed either qualitatively or quantitatively by any one of a number of accepted procedures.

REAGENTS

Ammonium thiocyanate, C. P., a saturated solution.

Hydrochloric acid, C. P., concentrated.

Lead nitrate, C. P., a solution containing 11.9 milligrams of lead per liter.

Methyl isopropyl ketone, Eastman Kodak, redistilled.

Potassium iodide, C. P., a saturated solution.

EXPERIMENTAL

A study of the extraction of the metal iodides revealed that a number of them were extractable into organic solvents. Those metals having iodides which were at least partially extracted into one or more of the organic solvents employed were bismuth, mercury, iron, lead, copper, palladium, cadmium, rhodium, gold and ruthenium. Among the organic solvents found to be useful in this extraction were butyraldehyde, n-amyl alcohol, methyl n-amyl ketone, methyl isobutyl ketone, methyl n-propyl ketone, methyl isopropyl ketone and ethyl acetate. After observing the solvent properties of these organic liquids, methyl isopropyl ketone was found to be the most desirable solvent because it was relatively inexpensive, highly effective in dissolving the metal iodides, did not tend to form emulsions, and was at most only partially miscible with water. This miscibility was reduced considerably in the presence of strong electrolytes such as potassium iodide, ammonium thiocyanate and hydrochloric acid, which were eventually used in the extraction.

The extraction of lead iodide from neutral solutions into methyl isopropyl ketone was incomplete as evidenced by flotation of the lead iodide precipitate in the organic phase. On the addition of hydrochloric acid, the precipitate was dissolved completely in the organic phase. It was found that lead iodide was most completely extracted from aqueous solutions containing 5% by volume of concentrated hydrochloric acid. The method employed in analyzing for lead was the modification of the

Fischer-Leopoldi method suggested by Winter and co-workers (1). In this case, as well as in the determination of the distribution ratio and the effect of iodide concentration upon the extraction, the aqueous phase was analyzed for lead. The Klett-Summerson Photoelectric Colorimeter was used in measuring the optical density of lead-dithizone solutions prepared in the analysis of lead throughout these experiments. A green filter was used to allow maximum transmission in the region of 540 millimicrons.

The distribution of lead between the organic and aqueous phases was determined after extraction and separation of the phases by analyzing the aqueous layer for lead content. The lead solution which was extracted contained 119 micrograms of lead, 3.75 milliliters of a saturated solution of potassium iodide and 1.25 milliliters of concentrated hydrochloric acid, diluted to 25 milliliters. This solution was shaken in a 60 milliliter separatory funnel with 25 milliliters of methyl isopropyl ketone which had been previously saturated with 5% hydrochloric acid, and one hour was allowed for equilibrium to be reached between the phases. The aqueous phase was then passed into a 60 milliliter pyrex separatory funnel and its lead content determined by the dithizone method previously mentioned. It was found that 4 micrograms of lead remained in the aqueous phase after extraction, thus providing a distribution ratio of 28.8/1, or an extraction which is 97% complete in one pass.

In attempting to determine the effect of iodide ions upon the distribution ratio a very interesting phenomenon was observed. A series

of aqueous solutions was prepared containing 5% by volume of concentrated hydrochloric acid and 119 micrograms of lead. These were treated with potassium iodide sufficient to provide ratios of lead ions to iodide ions of 1:10, 1:100, 1:1000 and 1:10000. In Table 1. is found a tabulation of the results of extracting these solutions with methyl isopropyl ketone previously saturated with 5% hydrochloric acid.

Since a considerable quantity of iodine was liberated from the more concentrated iodide solutions and extracted into the organic layer, it was thought that this free iodine may possibly have been responsible for the more complete extraction of lead. However, by adding iodine to the weaker iodide solutions and extracting, no change was brought about in the distribution ratio. It was thought possible that the presence of an excess of strong electrolyte in the more concentrated iodide solutions might have an enhancing effect upon the degree to which lead iodide was extracted. This was tested by adding potassium nitrate, a non-interfering electrolyte, to the weaker iodide solutions to be extracted. Results indicate some effect but there was insufficient evidence to establish that excess electrolyte was responsible for the more favorable distribution ratio.

A preliminary interference study was next conducted to determine which ions were extracted as their iodides from acidic aqueous solutions. For this study the ions were grouped as indicated in Table II. The ions are presented in their more common forms although it is realized that in many cases they exist as complexes. One milliliter of a 1% solution of each

ion was used. To each group were added 1 milliliter of a saturated solution of potassium iodide and sufficient concentrated hydrochloric acid to make the solution 5% with respect to acid. Each solution was then shaken thoroughly in a separatory funnel with 5 milliliters of methyl isopropyl ketone, and after allowing time for phase separation the aqueous phase was discarded. The organic layer was concentrated to approximately 1 milliliter by evaporation and a spectrographically pure carbon electrode (National Carbon Company) was soaked in the solution for two hours. The electrodes prepared in this manner were dried in an oven for 30 minutes at 110°C. and then analyzed by means of a Bausch and Lomb Large Littrow Spectrograph. Examination of the plate resulting from this analysis revealed partial extractions of the ions as shown in Table II.

A second series of solutions was prepared consisting of the above groups of ions and each containing 1 milliliter of 1% lead solution. These solutions were treated and analyzed as before. From a study of the resulting spectrogram it was found that in the presence of lead, rhodium and ruthenium were extracted quite well, though otherwise their extraction was slight. A similar but less significant influence was exerted by lead upon the extraction of platinum.

A previous observation of the extraction of the iodides of iron, bismuth, mercury, palladium and gold had definitely established those ions as interferences in the extraction of lead iodide by methyl isopropyl ketone. Therefore, to avoid the complexity which the spectral

lines of those elements, particularly iron, would have introduced, they were not included in the spectrographic study.

Although the solubility of a number of the metal thiocyanates in organic solvents is well known, the utilization of this fact as a means of removing interferences due to those ions is not a widely used procedure. Iron, copper, zinc, mercury, gold and palladium can be completely extracted into methyl isopropyl ketone from acidic aqueous solutions containing thiocyanate ions. At the same time, lead is unaffected by such an extraction. Antimony and tin are extractable from hydrochloric acid solutions, so by employing a preliminary extraction with thiocyanate and hydrochloric acid, most of the interferences in the extraction of lead iodide were removed. After this preliminary extraction had been performed, potassium iodide was added and the solution was shaken with an additional portion of solvent.

In order to determine the effectiveness of such a procedure in isolating lead, a spectrographic study was made similar to the one described in a previous paragraph. The ions to be studied were grouped according to Table III. To each group was added 1 milliliter of a saturated solution 5% in hydrochloric acid. After separation of phases, 1 milliliter of a saturated solution of potassium iodide was added to the aqueous phase, and this solution was then thoroughly shaken with 5 milliliters of methyl isopropyl ketone. After separation of the phases, the organic phase was evaporated to a volume of about 1 milliliter. The electrodes

were soaked in the solution thus obtained for 2 hours, dried for an hour at 110°C, and finally analyzed by means of the Large Littrow Spectrograph. An examination of the resultant spectrograms revealed the only interferences to be cadmium and ruthenium.

DISCUSSION AND CONCLUSIONS

The extraction of lead into methyl isopropyl ketone was found to have a very favorable distribution ratio when the proper acidity was maintained and a considerable excess of iodide ions was present in the system. The effect of iodide ion concentration upon the distribution ratio was significant in that a ratio of iodide ions to lead ions much greater than the stoichiometric ratio of these ions in known lead compounds was required for optimum extraction.

The use of a preliminary extraction to remove the interferences accomplishes the purpose neatly and efficiently without adding materially to the time required to complete the isolation of lead. The time consuming, relatively cumbersome techniques of precipitation were thus avoided.

Since the extraction of lead iodide did not produce a highly colored organic phase, the method did not lend itself to use in a direct colorimetric procedure. However, by virtue of its favorable distribution ratio and high selectivity, the extraction should find application as a means of isolating lead for analysis by standard procedures.

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TABLE I.

The Effect of Iodide Ion Concentration on the Distribution Ratio

Ratio of Pb^{++} to I^-	Distribution Ratio
1:10	0/1
1:100	0.21/1
1:1000	1.48/1
1:10000	8.95/1

TABLE II.

Ions Included in the Preliminary Interference Study

Group 1	Group 2	Group 3	Group 4
Ca^{++}	$*Zn^{++}$	$*As^{+++}$	$*Rh^{+++}$
Ba^{++}	$*Cd^{++}$	$*Sb^{+++}$	$*Ru^{+++}$
Sr^{++}	Co^{++}	$*Sn^{++++}$	$*Pt^{++++}$
Mg^{++}	Ni^{++}	Al^{+++}	Os^{++++}
	$*Cu^{++}$	Cr^{+++}	Ir^{++++}

* Partially extracted

TABLE III.

Ions Included in the Final Interference Study

Group 1	Group 2	Group 3	Group 4	Group 5	Group 6	Group 7
Cu^{++}	Zn^{++}	Sb^{+++}	Bi^{+++}	Pt^{++++}	Pd^{++}	Ru^{+++}
Fe^{+++}	Cd^{++}	Sn^{++++}	Hg^{++}	Au^{+++}	Rh^{+++}	Pb^{++}
Pb^{++}	Pb^{++}	Pb^{++}	Pb^{++}	Pb^{++}	Pb^{++}	

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Specific Spot Test for Gold Employing Pararosaniline Hydrochloride

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Specific Spot Test for Gold Employing Pararosaniline Hydrochloride

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AS A RESULT of the studies of West and Amis (*11*) of the reaction of pararosaniline hydrochloride with palladous ion, it was found that gold reacted with the reagent in such a manner as to suggest definite possibilities for use as a spot test for gold. Further investigation revealed that the reaction, the nature of which has been established by West (*9*), had a sensitivity comparable with other tests for gold described in the literature (*2–4, 7, 8*). In addition, the selectivity of the reaction was found to be far superior to most reactions involving gold, and on this basis showed special promise for spot test work.

REAGENTS

Pararosaniline hydrochloride, 0.05% aqueous solution. Ethyl acetate, C.P.

Tetrasodium pyrophosphate. Saturated solution adjusted to *p*H 7.0 with hydrochloric acid (prepared fresh each day).

Hydrochloric acid, C.P. (concentrated).

EXPERIMENTAL

Of the media commonly employed in spot test analysis, filter paper holds an advantage over the spot plate for use in this test because the reaction sensitivity was found to be greater using certain papers than when test tubes or spot plates were employed. The effect of using different grades of filter paper on sensitivity was found to vary to a remarkable degree, the greatest sensitivity being afforded by Schleicher and Schüll No. 595 filter paper. Diffusion of 0.05% pararosaniline hydrochloride (Schultz No. 511 from the National Aniline and Chemical Company) through this paper leaves a concentration of the reagent in the form of a ring about 7 mm. in diameter with only slight diffusion of the reagent beyond this point. Diffusion of the reagent in other papers was sometimes faster, but distribution of the reagent in those cases did not leave the ring of concentrated reagent in which the violet-black precipitate of gold fuchsin is most easily discernible when gold is to be detected in small amounts.

The order of spotting of reagent and test solution was found to be important, because gold, when spotted on paper, was apparently adsorbed so strongly that it reacted only slowly with reagent which was subsequently added to the spot. When the order of spotting was reversed, the reaction took place quickly with maximum sensitivity.

Interference studies were made according to the general procedure described by West (*10*), and palladium, rhodium, platinum, and mercurous mercury were found to react with the fuchsin in a manner analogous to gold. Attempts to eliminate these interferences were made using such complexers as ammonia, cyanide, thiocyanate, ethylenediaminetetraacetic acid, pyridine, aniline, malonate, tartrate, and citrate. In those cases where complexation of interferences was successful, gold was also masked so strongly as to prevent its reaction with pararosaniline, except that pyrophosphate was effective in sequestering palladium without adversely affecting the reactions of gold. Inasmuch as the complexation of the other interfering ions could not be effected through the use of pyrophosphate, other means were sought by which these interferences could be eliminated and specificity attained.

Lenher (*5*) reported that gold can be extracted from aqueous solutions by many organic compounds, the esters and particularly ethyl acetate being most efficient for this separation. Later Lenher and Kao (*6*) showed that maximum separation was obtained when the aqueous solutions contained hydrochloric acid in concentrations of 10% by volume. Because these extraction techniques seemed promising, an investigation was undertaken to determine the feasibility of adapting them to spot test procedures. By using a dropper pipet for extraction and phase separation, an elegant method was developed which serves to isolate gold from all potential interfering ions. [Although a medicine dropper can be used, a modified pipet (*1*) provides more thorough mixing and sharper separation of phases.] Such a procedure not only serves to prevent interferences but affords a simple, rapid method of concentrating gold from relatively dilute test solutions. In practice, the extraction involves the addition of a few drops of extractant to one or more drops of the test solution. Thorough mixing of the aqueous layer and ethyl acetate is then accomplished by drawing them into and expelling them from the dropper pipet several times, finally drawing both layers into the dropper and allowing a short time for phase separation. After the aqueous layer is disposed of, the ethyl acetate layer is added to a spot plate depression or a microbeaker where the solvent is evaporated. The auric chloride is then put into solution by means of a drop of saturated sodium pyrophosphate which serves to complex any

Table I. Scope of Interference Studies

Na^+	Be^{++}	BO_2^-	CO_3^{--}	NH_4^+	S^{--}	F^-	Fe^{++}	CN^-
Li^+	Mg^{++}	$B_4O_7^{--}$	SiO_3^{--}	NO_2^-	$S_2O_3^{--}$	Cl^-	Fe^{+++}	$Fe(CN)^{----}$
K^+	Ca^{++}	Al^{+++}	Ti^{++++}	NO_3^-	SO_3^{--}	ClO_3^-	Co^{++}	$Fe(CN)^{---}$
Cu^{++}	Zn^{++}	Sc^{+++}	GeO_3^{--}	$H_2PO_2^-$	SO_4^{--}	ClO_4^-	Co^{+++}	CNS^-
Rb^+	Sr^{++}	Ga^{+++}	Sn^{++}	HPO_3^{--}	Cr^{+++}	Mn^{++}	Ni^{++}	Acetate
Ag^+	Cd^{++}	Y^{+++}	Sn^{++++}	$P_4O_{13}^{------}$	$Cr_2O_7^{--}$	MnO_4^-	Ru^{+++}	Oxalate
Cs^+	Ba^{++}	In^{+++}	Pb^{++}	$P_6O_{18}^{------}$	CrO_4^{--}	Br^-	Rh^{+++}	Malonate
	Hg^+	La^{+++}	Zr^{++++}	PO_3^-	SeO_3^{--}	BrO_3^-	Pd^{++}	Adipate
	Hg^{++}	Ce^{+++}	Th^{++++}	HPO_4^{--}	SeO_4^{--}	I^-	Os^{+++}	Succinate
		Tl^+		$P_2O_7^{----}$	MoO_4^{--}	IO_3^-	Ir^{++++}	Phthalate
				V^{+++}	TeO_3^{--}	ReO_4^-	Pt^{++++}	Tartrate
				VO_3^-	TeO_4^{--}			Citrate
				$HAsO_3^{--}$	WO_4^{--}			Lactate
				$HAsO_4^{--}$	UO_2^{++}			Gluconate
				Sb^{+++}	UO_4^{--}			Glycol
				Sb^{+++++}				Diethylene glycol
				Bi^{+++}				Inositol
								Sorbitol
								Mannitol
								Sucrose
								Dextrose
								Aniline
								Pyridine

traces of palladium that might have been carried over because of incomplete separation.

RECOMMENDED TEST PROCEDURE

Place 1 drop to 1 ml. of test solution in a spot plate depression or microbeaker and add one tenth as much concentrated hydrochloric acid. Then add 10 to 15 drops of C.P. ethyl acetate and with a dropper pipet draw and expel the mixture six to eight times, finally drawing the contents into the pipet. Allow a few seconds for separation of the two layers and discard the aqueous layer. Wipe the tip of the pipet with filter paper and expel a small drop of the ethyl acetate solution while the tip is pressed against the paper, then transfer the remaining contents of the pipet to a second depression or microbeaker. Invariably a small drop of the aqueous layer adheres to the tip of the pipet and is released with the last drop of the ethyl acetate in the pipet. For this reason it is recommended that the final drop of ethyl acetate be retained in the pipet. By means of a piece of glass drawn into a fine tip, blow into the ethyl acetate until it has evaporated and add one drop of saturated tetrasodium pyrophosphate. Put one drop of 0.05% pararosaniline hydrochloride solution on Schleicher and Schüll No. 595 filter paper and as soon as the reagent is absorbed place the test drop in its center.

If the test drop is spotted into the reagent drop carefully it will form a convex surface with the ring of concentrated reagent as its boundary and diffusion of the test drop takes place through this ring. When gold is present in small amounts it is precipitated in the ring as a violet-black precipitate, and when present in large amounts the test color is a deep brown. The limit of identification employing this procedure is 5 micrograms of gold at a limiting concentration of 1 part in 100,000 (based on 0.5-ml. volume of test solution).

REMARKS

Interference studies were made using 1% solutions of the ions to be tested, in the presence of 0.01% gold, thus providing a ratio of interfering ion to gold of 100 to 1. The ions investigated in the interference studies are listed in Table I in their more common forms. In many instances the ions concerned are present as complexes, but where structures of such complexes may be in doubt, only the valence of the central atom is indicated.

The conditioned reaction showed no positive interferences and the only negative (masking) interferences were those given by cyanides and sulfides. The use of pyrophosphate ion to complex palladium provides a method of sequestering that ion so effectively that it is not precipitated by dimethylglyoxime and reacts with iodide only slowly to give the characteristic brown complex. Failure to eliminate the interferences of rhodium, platinum, and mercurous mercury made the use of pyrophosphate impractical for general work. In those cases in which palladium constitutes the only serious interference, pyrophosphate is an invaluable sequestrant and permits the simplification of the test by eliminating the necessity of using the extraction procedure.

Solutions of pararosaniline hydrochloride should be prepared fresh about once a month, for if allowed to stand for longer periods of time they may prove ineffective in detecting amounts of gold near the limit of identification. Freshly prepared solutions of chloroauric acid gave a much better response to the reagent than those which had been standing in the laboratory for some time.

To increase the sensitivity of the test numerous filter papers were tried, including Schleicher and Schüll Nos. 497, 589, 590, 595, 597-Y, and 604; Whatman Nos. 1, 2, 4, 5, 30, 40, 41, 42, 44, 50, and 120; Reeve-Angel Nos. 201 and 202; E&D (Chicago Apparatus Co.) Nos. 615 and 618. The paper found to be most satisfactory for this test was S. & S. No. 595, for it not only possessed excellent absorption characteristics but also was found to be of very uniform quality.

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Extraction Pipet for Spot Test Analysis

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Extraction Pipet for Spot Test Analysis. Jack K. Carlton,
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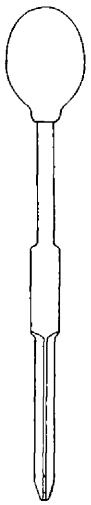
IN ORDER to apply extraction techniques to spot test analysis and preserve the essence of the spot test method, a small and simple device was needed, in which the component liquids could be thoroughly mixed and allowed to separate as rapidly as possible. A dropper pipet, with a few modifications, satisfied these requirements.



The pipet consists of a capillary tip 6 cm. long, 7 mm. in outside diameter, and 1.8 mm. in inside diameter; a bulb blown just above the capillary tip, 4 cm. long, 1.15 cm. in outside diameter, and about 2- to 3-ml. capacity; an upper stem 5 cm. long, 7 mm. in outside diameter, and 5 mm. in inside diameter; and a rubber bulb of 10-ml. capacity. The over-all length of the pipet is approximately 15 cm. None of these dimensions is critical. When low boiling liquids such as ether, chloroform, carbon tetrachloride, and carbon disulfide are used as extractants, a capillary of about 0.7- or 0.8-mm. bore is recommended.

Mixing is accomplished by drawing the liquids into the pipet and then expelling them, repeating the procedure several times, quickly. By using a rubber bulb of considerably greater capacity than that of the pipet, a large quantity of air is drawn into the pipet after the liquids have been drawn up, and the bubbling of this air through the two liquid layers provides a very efficient mixing of the two layers.

Care should be exercised in using the pipet to avoid the loss of the liquids being mixed. When the liquids are drawn into the pipet the pressure of the fingers on the rubber bulb should be released slowly, so that when the air begins to bubble through, the liquids will not spatter into the rubber bulb or on the sides of the upper stem, to which droplets might adhere and consequently be lost. On expulsion, pressure should be applied to the rubber bulb slowly to avoid spattering when the air begins to bubble through the liquids which have been passed into a small beaker.

The use of extraction techniques in spot test analysis offers a means of separating an ion from its interferences which might prove valuable in a manner similar to the use of masking agents. West and Carlton [(ANAL. CHEM., 22, 1055 (1950)] use such an extraction in separating gold from the platinum metals. For such work the extraction pipet described should find useful application.

The author wishes to express his appreciation for financial assistance given him under a contract with the Office of Naval Research.

SUMMARY

1. A systematic study has been made of the extraction of metal complexes with organic solvents. Some of the less familiar solvents were included in the survey in order to determine their value as solvents in the extraction of metallic complexes. Methyl isopropyl ketone and butyraldehyde proved to be very good solvents.
2. The iodide, chloride and thiocyanate complexes of several of the metal ions were found to extract quite well into some of the solvents employed in the study.
3. A detailed investigation was made of one of the systems in the extraction study, the extraction of lead iodide by methyl isopropyl ketone.
4. It was found that lead ions, when treated with a large excess of iodide ions and adjusted to the proper acidity, were extracted quantitatively into methyl isopropyl ketone. Interferences were minimized by performing a preliminary extraction with methyl isopropyl ketone after conditioning with ammonium thiocyanate and hydrochloric acid.
5. A spot test for gold was developed employing pararosaniline hydrochloride as reagent. Specificity was attained through the use of an extraction procedure by means of which gold was isolated from its interferences. The test was sensitive to 5 gamma of gold.
6. An extraction pipet was designed to facilitate extraction and separation of small quantities of materials.

VITA

Jack Kenneth Carlton was born October 6, 1921 in Baileyville, Texas. He received his elementary and high school education in the public school system of Shreveport, Louisiana. He was graduated from Centenary College of Shreveport in June of 1942 with a B. S. in Chemistry. After graduation he was employed by the Chemical Warfare Service as P-1 and P-2 chemist for fifteen months before volunteering for service in the Navy. He received an honorable discharge in June of 1946 and entered the graduate school of Louisiana State University the following September. He was awarded the degree of Master of Science in Chemistry on June 4, 1949. He has held teaching assistantships for two years and for the past two years has held a research fellowship sponsored by the Office of Naval Research.

He was married to Mary Ellen Petree on June 1, 1948 and now has two daughters.

He is at present a candidate for the degree of Doctor of Philosophy.

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Major Field: Chemistry

Title of Thesis: Studies on the Application of Extraction Methods to Analytical Chemistry

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